

Assessment of the Critical Load of Trace Elements in Soils Polluted by Pyrite tailings. A Laboratory Experiment

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Abstract Nineteen soil samples (SE Spain) with very different chemical physical properties and developed over different parent materials were contaminated by adding increments of an acidic solution from oxidised pyrite tailings. The quantities of Cu, Zn, Cd and Pb precipitated by the soil samples were directly and significantly related to the pH-buffering capacity. However, when the contamination caused the pH to fall below 3.0 the soil tended to release a fraction of the element adsorbed, which increased as the pH decreased. The quantity of each precipitated element at which the action value for each element is reached, was also directly related to the pH-buffering capacity. Nevertheless, in carbonate-rich soils, the precipitated Cu and Zn maintained a relatively high level of bioavailability, while Cd reached a critical level with a content exceeding 25 mg kg^{-1} , regardless of the pH-buffering capacity.

Keywords Soils · Pyrite tailings · Trace elements · Buffering capacity · Critical Load · pH

1 Introduction

Under natural conditions, the concentration of trace elements in the soil is relatively low, but certain human actions, such as agriculture, (Kabata-Pendias 1995), the application of tailings with residues when used as an organic amendment (Plaquart et al. 1999; McBride 2003), the application of solid urban waste as fertiliser, atmospheric particle transport (Alloway 1995; Föstner 1995), as well as mining (Egger 1994; Ripley et al. 1996; Vartanyan 1989), mining accidents (Cabrera et al. 1999; Simón et al. 1998) or continuous atmospheric depositions (Nicholson et al. 2003) can raise contamination above toxic levels. In these cases, the soil is capable of attenuating the mobility of diverse contaminants by, for example, filtration, neutralisation, adsorption and precipitation; these processes inactivate potential toxicity, blocking undesired elements from passing to more sensitive systems such as the air or water. The capacity of each soil to retain metals depends on the soil properties, mainly texture, organic-matter content, ion-exchange capacity, oxide contents, pH, specific surface area and carbonate content (Alloway 1995; Ross 1994). When this capacity is exceeded, the soil ceases to be effective as the protector of the ecosystem (sink) and can even function as a source of toxic substances. The critical load represents “the maximum quantity of a given contaminant that can be supplied to a soil without causing chemical changes leading to long-term harmful effects on ecosystem structure and function” (Hettelingh et al. 1991).

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This study was aimed at estimating the critical load of soils with different properties withstanding a contaminating solution resulting from the oxidation of pyrite tailings with a pH value lower than 2.0 and containing a high concentration in trace elements such as Cu, Zn, Cd and Pb. This estimation can be made as a function of: (a) maximum concentration of Cu, Zn, Cd and Pb that precipitate in each soil within the range of pollution considered in this study (MPC, maximum precipitated concentration), (b) concentration of precipitated elements at which action values (AV, action values) or values above which plants and soil solution should be watched (Prüeß 1997), are reached (CAV).

When the soil concentration of a certain contaminant approaches the MPC, not only does it exceed its critical load and affect the functioning of the ecosystem, but new additions could reach surface waters and groundwater whereupon the contamination would spread to other ecosystems. At the same time, given that the precipitated elements may remain in bioavailable form, before the MPC is reached, the AV may be reached, at which point the soil would be expected to begin to display harmful effects. Therefore, the structure and functioning of the ecosystem would begin to be visibly affected when the soil reaches the AV, whereas when it reaches the MPC the surrounding ecosystems would also be visibly affected.

2 Materials and Methods

2.1 Soil Properties

The soil samples belong to the provinces of Granada and Jaen located in the southeast of Spain. The selected soil samples represent a heterogeneous range of soils with different chemical properties and developed over different parent materials (Table 1).

Soil samples were air dried and then screened to 2 mm to analyse them. Particle size distribution was determined by the pipette method after elimination of organic matter with H_2O_2 and dispersion with sodium hexametaphosphate (Loveland and Whalley 1991). The pH was measured potentiometrically in a 1:2.5 soil–water and soil 0.1 mol l^{-1} KCl suspension. The calcium carbonate equivalent content (CaCO_3 , %) was determined by the method of Bascomb (1961). Total carbon was analysed by dry combustion with a LECO SC-144DR instrument. Organic carbon (OC)

was determined by the difference between total carbon and inorganic carbon from CaCO_3 . The cation-exchange capacity (CEC) was determined with 1 M Na acetate at pH 8.2, measuring sodium in a Meteor NAK-II flame-photometer. Exchange bases were determined with 1 M H_4N acetate at pH 7.0, measuring sodium and potassium in a Meteor NAK-II flame-photometer and calcium and magnesium by atomic absorption spectrometry in a Varian SpectrAA 220FS machine, the specific surface area (SA) determined by weighing the water adsorbed by the sample from a solution saturated with CaCl_2 (Keeling 1961); total iron (Fe_d) and aluminium (Al_d) oxides and oxi-hydroxides of the soil samples were extracted with citrate-dithionite (Holmgren 1967).

2.2 Contaminating Solution (CS)

Ten grams of pyrite tailings from the mining spill at Aznalcóllar (Seville, Spain) were placed in contact for 3 days with 1,000 cm^3 of H_2O_2 at 15%. The contaminating solution (CS) presented a pH of 1.7 and a concentration in Cu, Pb, Zn and Cd of 14.5, 3.2, 55.4 and 0.21 mg dm^{-3} , respectively (more details of the contaminating solution composition is given in Simón et. al. 1999).

2.3 Spiked Soils

According to their properties, different quantities of CS were added to soil samples. Thus, 1, 1.5, 2, 3 and 5 cm^3 CS g^{-1} were added to the sandy and acid soils ($\text{pH} < 7.0$); 1, 2, 4, 6 and 10 cm^3 CS g^{-1} were added to soils with a sandy-loam texture or finer and $\text{pH} > 7.0$ and $\text{CaCO}_3 < 2\%$; 2, 6, 10, 15 and 20 cm^3 g^{-1} were added to soils with a loamy texture or finer, $\text{pH} > 7.5$ and CaCO_3 between 2% and 30%; and 10, 20, 30, 40 and 50 cm^3 g^{-1} were added to soils with a loamy texture or finer, $\text{pH} > 8.0$ and $\text{CaCO}_3 > 30\%$. After 72 h of shaking (Alonso et al. 1997), each soil extract–CS was measured for pH and centrifuged at 3,000 rpm for 15 min, separating the solid and liquid fractions.

2.4 Total Water and NH_4NO_3 Extractable Trace Element Concentrations

To determine water soluble forms, soil–water extracts were prepared in a ratio 1:10 (Norma DIN 38 414-4)

Table 1 Physico-chemical properties of the studied soils

| Samples | Parent material | pH _{H2O} | pH _{KCl} | CaCO ₃ (%) | M.O. (%) | cmol _c kg ⁻¹ | | | V (%) |
|---------|-----------------|-------------------|-------------------|-----------------------|----------|------------------------------------|------|-------|-------|
| | | | | | | Ca | Mg | CEC | |
| J-1 | Quartzite | 6.90 | 5.90 | 0.20 | 1.62 | 2.50 | 0.58 | 3.51 | 35.4 |
| J-2 | Sandstone | 6.80 | 5.50 | 0.70 | 0.96 | 4.25 | 0.82 | 5.62 | 85.8 |
| J-3 | Granite | 5.70 | 4.10 | 0.80 | 5.06 | 2.75 | 0.41 | 8.79 | 46.2 |
| J-4 | Slate | 6.40 | 4.40 | 0.10 | 1.98 | 6.75 | 2.88 | 7.73 | 100 |
| Gr-1 | Filite | 8.20 | 7.20 | 3.30 | 2.50 | 6.00 | 2.99 | 5.62 | 100 |
| Gr-2 | Conglomerate | 6.60 | 4.70 | 1.00 | 1.01 | 10.87 | 3.67 | 16.17 | 77.8 |
| Gr-3 | Limestone | 8.00 | 7.00 | 0.40 | 8.70 | 23.00 | 1.16 | 24.6 | 78.1 |
| Gr-4 | Schist | 7.60 | 6.20 | 0.60 | 3.69 | 9.50 | 2.66 | 12.65 | 100 |
| Gr-5 | Schist | 7.70 | 6.60 | 0.70 | 1.93 | 6.50 | 1.08 | 7.03 | 96.5 |
| Gr-6 | Conglomerate | 8.30 | 7.10 | 0.60 | 1.74 | 16.21 | 2.49 | 18.98 | 100 |
| Gr-7 | Limestone | 7.80 | 6.90 | 0.90 | 7.90 | 28.00 | 1.49 | 30.93 | 74.7 |
| Gr-8 | Filite | 8.30 | 7.50 | 19.60 | 5.77 | 12.25 | 5.06 | 15.42 | 83.9 |
| Gr-9 | Limestone | 8.40 | 7.20 | 5.10 | 2.39 | 27.00 | 1.33 | 16.17 | 100 |
| Gr-10 | Evaporite | 7.80 | 7.50 | 56.50 | 1.90 | 41.89 | 4.32 | 13.71 | 100 |
| Gr-11 | Limestone | 8.20 | 7.40 | 22.90 | 2.71 | 30.50 | 1.91 | 18.98 | 100 |
| Gr-12 | Limestone | 8.20 | 7.50 | 59.00 | 3.34 | 27.25 | 1.49 | 15.47 | 100 |
| Gr-13 | Marl-Limestone | 8.40 | 7.20 | 79.60 | 0.85 | 24.25 | 1.00 | 13.36 | 100 |
| Gr-14 | Dolomite | 8.20 | 7.50 | 32.60 | 3.08 | 10.00 | 3.24 | 11.25 | 100 |
| Gr-15 | Dolomite | 8.30 | 7.30 | 84.60 | 1.90 | 4.25 | 3.15 | 12.30 | 100 |

| Sample | % Sand | % Silt | % Clay | SE (m ² /g) | Fe _d % | BC _{3,5} (cmolH ⁺ kg ⁻¹) |
|--------|--------|--------|--------|------------------------|-------------------|---|
| J-1 | 59.30 | 28.00 | 12.70 | 4.54 | 0.34 | 0.62 |
| J-2 | 66.30 | 19.20 | 14.50 | 13.73 | 0.73 | 0.39 |
| J-3 | 78.00 | 14.00 | 8.00 | 17.66 | 0.26 | 0.47 |
| J-4 | 57.40 | 32.00 | 10.60 | 34.81 | 0.92 | 0.85 |
| Gr-1 | 58.80 | 23.30 | 17.90 | 14.03 | 0.87 | 8.36 |
| Gr-2 | 32.50 | 13.30 | 54.20 | 108.45 | 2.10 | 1.14 |
| Gr-3 | 60.80 | 16.10 | 23.10 | 69.27 | 0.76 | 8.28 |
| Gr-4 | 67.60 | 21.30 | 11.10 | 43.86 | 0.87 | 1.93 |
| Gr-5 | 68.10 | 19.20 | 12.70 | 19.45 | 1.55 | 2.91 |
| Gr-6 | 33.60 | 15.60 | 50.80 | 100.56 | 2.83 | 5.81 |
| Gr-7 | 23.60 | 55.80 | 20.60 | 111.88 | 2.49 | 16.14 |
| Gr-8 | 49.80 | 28.30 | 21.90 | 32.78 | 1.02 | 17.76 |
| Gr-9 | 41.20 | 27.30 | 31.50 | 76.51 | 1.84 | 20.07 |
| Gr-10 | 22.40 | 55.70 | 21.90 | 43.68 | 0.21 | 90.83 |
| Gr-11 | 43.60 | 31.60 | 24.80 | 78.47 | 0.84 | 79.52 |
| Gr-12 | 38.80 | 37.10 | 24.10 | 54.58 | 0.55 | 82.49 |
| Gr-13 | 22.40 | 41.00 | 36.60 | 62.80 | 0.26 | 81.79 |
| Gr-14 | 40.80 | 33.60 | 25.60 | 29.78 | 1.10 | 63.34 |
| Gr-15 | 38.30 | 58.10 | 3.60 | 3.58 | 0.21 | 50.31 |

Soil samples are labelled according to the location of the sampling site (Jaen province, J and Granada province, Gr)

M.O. organic matter, *Ca* exchangeable calcium content, *Mg* exchangeable magnesium content, *CEC* cation-exchange capacity, *V* base saturation percentage, *Ss* Specific surface, *Fed* iron oxides

and then Cu, Pb, Zn and Cd water extractable concentrations were analysed. Trace element precipitated concentrations (MPC) were determined as the difference between trace element concentration in the CS and water extractable concentration measured in soil water extracts. Finally, the pH value measured in the soil–water extracts. Soils were also analysed for the trace element concentrations extractable by NH_4NO_3 1 M (DIN 19730; Pr     1997). In all cases, the concentration of the different metals (Cu, Zn, Cd and Pb) was measured by ICP-MS in a PE SCIEX ELAN-5000 A spectrometer.

Distribution coefficients (K_d) represent the sorption affinity of the soil solid phase for trace elements in solution and can be used as a valuable tool to study metal-cation mobility and retention in soil systems. The distribution coefficients (K_d), ratios between the quantity of precipitated element (mmol kg^{-1}) and the quantity remaining in solution (mmol dm^{-3}), were calculated according to Alloway (1995). According to Anderson and Christensen (1988), high K_d values indicate that the metal has been retained by the solid phase through sorption reactions, while low values of K_d indicate that a large fraction of the metal remains in solution.

2.5 Determination of Buffering Capacity of Soils

The pH-buffering capacity of soils at $\text{pH}=3.5$ was evaluated ($\text{BC}_{3.5}$) as the cmol of H^+ needed to reduce soil pH value up to 3.5. The titration curves were drawn following the method of Hartikainen (1986), soil samples (air dried, <2 mm) were equilibrated with solutions of increasing concentrations of 10^{-3} M HCl (soil-solution ratio of 1:10) while maintaining the ionic strength constant. The suspensions were shaken for 60 min and then the pH measured after 4 days of settling; then the amount of H^+ added were plotted against the equilibrium pH values (titration curves). From these curves, the values for the acid neutralisation (BC) were determined graphically, this being referred to as the quantity of acid needed to bring the pH of the soil to a given value (Van Breemen et al. 1983). In the present study, the pH value of 3.5 ($\text{BC}_{3.5}$) was taken as the reference value, like one of the intervals defined by Ulrich (1981) for soils and reflects the aluminium and iron buffer region. Finally, the data were statistically processed using SPSS 12.0 software package.

3 Results and Discussion

3.1 pH-Buffering Capacity

The main property that marked a significantly different behaviour among the soils was the $\text{BC}_{3.5}$, which was related ($P<0.005$) to the calcium carbonate content ($\%\text{CaCO}_3$) and the sum of the exchangeable calcium and magnesium content in soils ($[\text{Ca}+\text{Mg}]$ expressed in $\text{cmol}_c \text{ kg}^{-1}$):

$$\text{BC}_{3.5} (\text{cmol H}^+ \text{ kg}^{-1}) = 0.792 \text{ CaCO}_3 + 0.870 [\text{Ca} + \text{Mg}]$$

$$r^2 = 0.903$$

indicating that the weathering of the carbonates and the exchange between basic cations (among which Ca and Mg are the most abundant) and protons are the main mechanisms controlling soil acidification. In any case, soils with different $\text{BC}_{3.5}$ values show similar pH-buffering capacity pattern in such a way that, based on this pattern, the soils were assigned to three groups (Fig. 1):

1. soils with $\text{BC}_{3.5} < 3 \text{ cmol H}^+ \text{ kg}^{-1}$, in which the pH value was reduced rapidly with the addition of CS, reaching pH values of 3.0 for additions of $\leq 2 \text{ cm}^3 \text{ CS g}^{-1}$ of soil;
2. soils with $\text{BC}_{3.5}$ between 3 and $20 \text{ cmol H}^+ \text{ kg}^{-1}$, in which the pH decreased gradually, reaching values of 3.0 for relatively lower concentration of contaminating solution (between 2 and $4 \text{ cm}^3 \text{ CS g}^{-1}$ of soil);
3. soils with $\text{BC}_{3.5} > 20 \text{ cmol H}^+ \text{ kg}^{-1}$, in which the decline of the pH was very gradual and in no case reached values of less than 6.5.

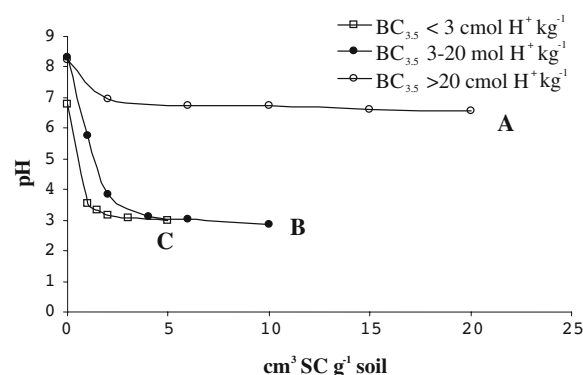


Fig. 1 Changes in pH values measured in H_2O of soils with different pH-buffering capacity at $\text{pH}=3.5$ ($\text{BC}_{3.5}$) with increasing amounts of contaminating solution added ($\text{cm}^3 \text{ SC g}^{-1}$ soil). (A) $\text{BC}_{3.5} > 20 \text{ cmol H}^+ \text{ kg}^{-1}$; (B) $\text{BC}_{3.5}$ between 3 and $20 \text{ cmol H}^+ \text{ kg}^{-1}$; (C) $\text{BC}_{3.5} < 3 \text{ cmol H}^+ \text{ kg}^{-1}$

3.2 Water-extractable Concentrations and Coefficient of Distribution

The coefficient of distribution (K_d), the ratio between the quantity of the precipitate of each element (mmol kg^{-1}) and the quantity that remained in solution (mmol dm^{-3}), revealed that the precipitation rate of the different trace elements was related to the $\text{BC}_{3.5}$. Thus, the greatest proportion of water extractable trace elements concentration was found in soils with $\text{BC}_{3.5} < 3 \text{ cmol H}^+ \text{ kg}^{-1}$ (Fig. 2 A), followed by those with $\text{BC}_{3.5}$ between 3 and $20 \text{ cmol H}^+ \text{ kg}^{-1}$ (Fig. 2 B); meanwhile, the greatest precipitation rate was registered for soils with $\text{BC}_{3.5} > 20 \text{ cmol H}^+ \text{ kg}^{-1}$ (Fig. 2 C). Similarly, the K_d values showed high solubility of Cd and Zn as opposed to Cu and Pb.

In general, within each of the defined groups, the quantity of precipitated metal tended to increase progressively with the ratio CS–soil extract until the maximum retention capacity of each soil (MPC), above which the precipitated metal concentration either tended to remain constant or tended to diminish. The first behaviour was noted in the soils with $\text{BC}_{3.5} > 20 \text{ cmol H}^+ \text{ kg}^{-1}$ (Fig. 3, Gr13), whereas the soils with $\text{BC}_{3.5} < 20 \text{ cmol H}^+ \text{ kg}^{-1}$ displayed the second behaviour (Fig. 3, Gr3). Therefore those soils with $\text{BC}_{3.5} < 20 \text{ cmol H}^+ \text{ kg}^{-1}$ could thus become a source of contamination when the MPC is exceeded (chemical time bomb; Stigliani 1988). In general, this

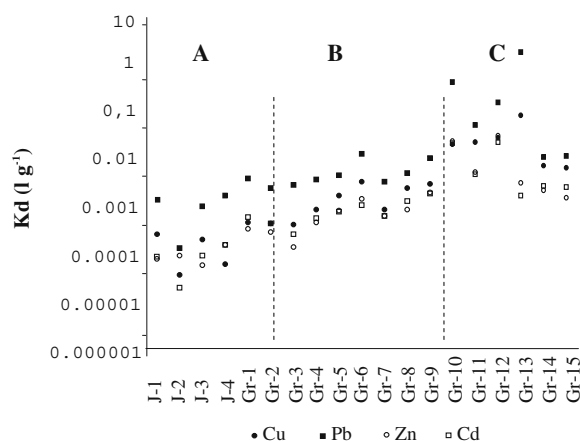


Fig. 2 Distribution coefficient for Cu, Pb, Cd and Zn in the studied soils, calculated at a dosage of 500 mg kg^{-1} of SC (K_{d500}). In the graph, we can distinguish between (A) K_{d500} of soils with $\text{BC}_{3.5} < 3 \text{ cmol H}^+ \text{ kg}^{-1}$; (B) K_{d500} of soils with $\text{BC}_{3.5}$ between 3 and $20 \text{ cmol H}^+ \text{ kg}^{-1}$; (C) K_{d500} of soils with $\text{BC}_{3.5} > 20 \text{ cmol H}^+ \text{ kg}^{-1}$

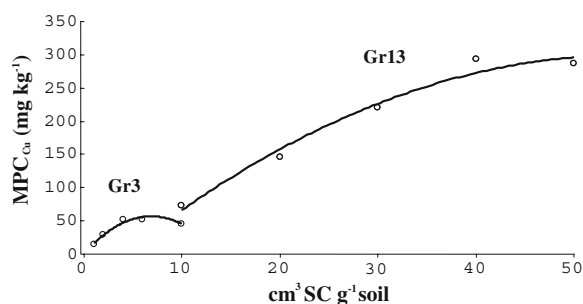


Fig. 3 Graph showing the precipitated concentration of copper with the increasing amount of metal (copper) added with the contaminating solution in soils Gr-3 (with $\text{BC}_{3.5} < 20 \text{ cmol H}^+ \text{ kg}^{-1}$) and Gr-13 (with $\text{BC}_{3.5} > 20 \text{ cmol H}^+ \text{ kg}^{-1}$)

process takes place in the studied soils when the pH of the soil extract–CS is less than or equal to 3.0.

In any case, these two types of behaviour should be understood within the range of the studied pollution, since at higher contamination rates even the pH of those soils with $\text{BC}_{3.5} > 20 \text{ cmol H}^+ \text{ kg}^{-1}$ could fall to values below 3.0, releasing precipitated elements and thus becoming in a potential threat to the ecosystem exposed to them.

Although MPC_{Cu} , MPC_{Pb} , MPC_{Zn} and MPC_{Cd} were significantly related ($p < 0.01$) to the $\text{BC}_{3.5}$, this relationship presented certain particularities, depending on the element. Thus, in the case of Cu, Zn and Cd, the relationship between the two parameters was linear:

$$\text{MPC}_{\text{Cu}} (\text{mg kg}^{-1}) = 11.84 + 3.11 \text{BC}_{3.5} (\text{cmol H}^+ \text{ kg}^{-1}) r^2 = 0.965$$

$$\text{MPC}_{\text{Zn}} (\text{mg kg}^{-1}) = 13.03 + 9.35 \text{BC}_{3.5} (\text{cmol H}^+ \text{ kg}^{-1}) r^2 = 0.955$$

$$\text{MPC}_{\text{Cd}} (\text{mg kg}^{-1}) = 0.124 + 0.02 \text{BC}_{3.5} (\text{cmol H}^+ \text{ kg}^{-1}) r^2 = 0.976$$

while Pb presented a different behaviour, depending on the value of the $\text{BC}_{3.5}$ (Fig. 4). When the $\text{BC}_{3.5} < 70 \text{ cmol H}^+ \text{ kg}^{-1}$, MPC_{Pb} was related logarithmically to $\text{BC}_{3.5}$ and tended to reach a constant value. When

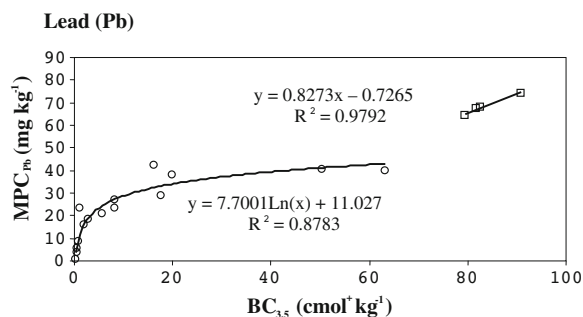


Fig. 4 Relationship between the maximum quantity of Pb precipitated (MPC_{Pb}) and the pH-buffering capacity ($\text{BC}_{3.5}$)

$BC_{3.5} > 70 \text{ cmol H}^+ \text{ kg}^{-1}$, as in the soils with a very high CaCO_3 content, the MPC_{Pb} tended to increase linearly.

3.3 Copper, Lead, Zinc and Cadmium NH_4NO_3 Extractable Concentrations

The relationship between the precipitated and the NH_4NO_3 1 M extractable concentration for each metal was established. From this relationship, we can deduce the quantity of precipitated metal at which the action level is reached (CAV) accepted by the DIN 19730 guidelines where AV are reported as 1 mg Cu kg^{-1} soil (AV_{Cu}), 3 mg Pb kg^{-1} soil (AV_{Pb}), 5 mg Zn kg^{-1} (AV_{Zn}) and $0.08 \text{ mg Cd kg}^{-1}$ soil (AV_{Cd}) (Prüß 1997). In all cases, the CAV value was also significantly related ($p < 0.01$) to the $BC_{3.5}$, although with certain particularities (Fig. 5). Thus, the CAV of Cu and Zn were related to the $BC_{3.5}$ through second-degree equations, differentiating among soils with $BC_{3.5} < 70 \text{ cmol H}^+ \text{ kg}^{-1}$ and $BC_{3.5} > 70 \text{ cmol H}^+ \text{ kg}^{-1}$. It is worth noting that the soils with $BC_{3.5} > 70 \text{ cmol H}^+ \text{ kg}^{-1}$ presented relatively low CAV values, indicating that, although the highly carbonate soils can precipitate high quantities of Cu and Zn, their bioavailability is high and can easily get into the food chain.

On the contrary, Cd and Pb did not differ. Thus, in all the soils, the CAV_{Cd} was related to the $BC_{3.5}$ according to the logarithmic equation in which there was a tendency for a steady value to be reached (Fig. 5c); this indicates, in general terms, that when the soils presented a Cd concentration of around 2.5 mg kg^{-1} , they exceeded the critical bioavailability level. In the case of Pb (Fig. 5d), the relation between CAV_{Pb} and $BC_{3.5}$ was exponential, so that an increase in the neutralisation capacity of soil acids allows a considerable increase in Pb before the critical bioavailability level is reached.

4 Conclusions

The calcium carbonate content together with exchangeable calcium and magnesium content are the main parameters regulating the buffering capacity as well as the critical load of the soils polluted by pyrite tailings. However, these parameters differ between the studied elements, Cu, Zn,

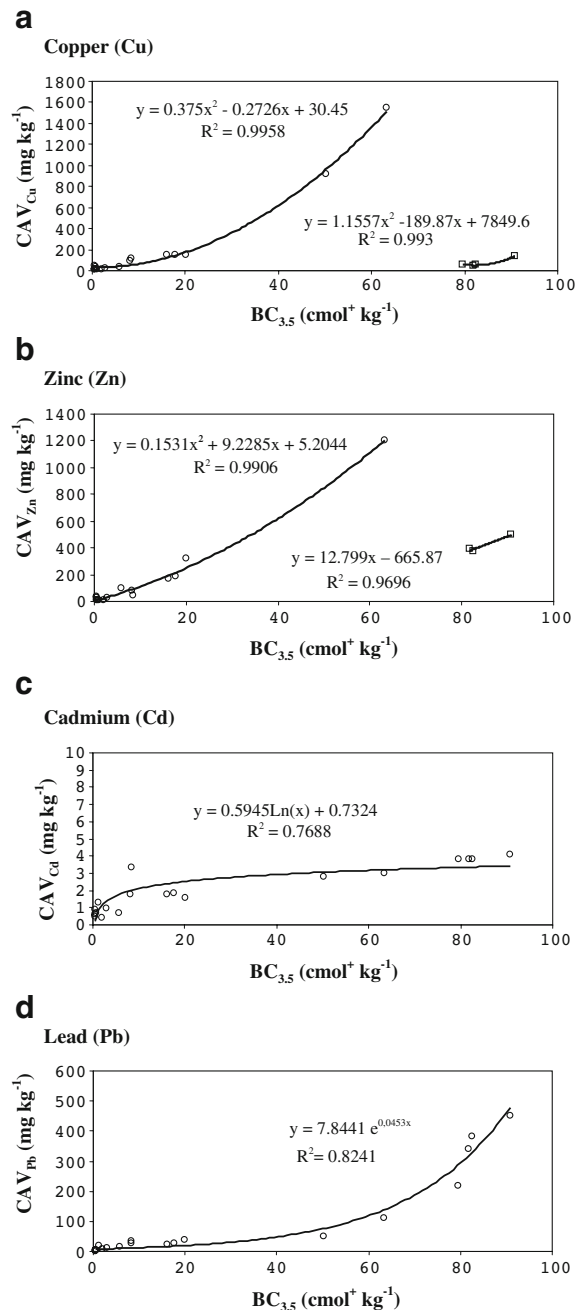


Fig. 5 Relationship between the quantity of metal precipitated (CAV_{Cu} and CAV_{Zn}) at which the action value (AV) is reached and the pH-buffering capacity at pH 3.5 ($BC_{3.5}$). Relationship between the quantity of metal precipitated (CAV_{Cd} and CAV_{Pb}) at which the action value (AV) is reached and the pH-buffering capacity at pH 3.5 ($BC_{3.5}$)

Cd and Pb in soils. Thus, while the NH_4NO_3 extractable Cu and Zn concentration tends to increase in highly carbonated soils, the Pb reduces drastically and the Cd tends to remain constant regardless of the soil characteristics.

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References

- Alloway, B. J. (1995). The origins of heavy metals in soils. In B. J. Alloway (Ed.), *Heavy metals in soils* (pp. 38–57). Blackie Academic and Professional.
- Alonso, I., Pérez, A. M., Moreno, A. M., & González, J. (1997). Retención de Zn, Cd, Pb y Cu después del proceso de adsorción-desorción. *Boletín de la Sociedad Española de la Ciencia del Suelo*, 3.1, 65–73.
- Anderson, P. R., & Christensen, T. H. (1988). Distribution coefficients of Cd, Co, Ni and Zn in soils. *Journal of Soil Science*, 39, 15–22.
- Bascomb, C. L. (1961). A calcimeter for routine use on soil samples. *Chemistry & Industry*, 45, 1826–1827.
- Cabrera, F., Clemente, L., Díaz Barrios, E., López, R., & Murillo, J. M. (1999). Heavy metal pollution of soils affected by the Guadamar toxic flood. *The Science of the Total Environment*, 242, 117–129.
- Egger, R. G. (1994). Mining and the environment: an introduction and overview. In R. G. Eggert (Ed.), *Mining and the environment: International perspectives on public policy* (pp. 1–20). Washington DC: Resources for the Future.
- Föstner, U. (1995). Land contamination by metals: global scope and magnitude of problem. In H. E. Allen, C. P. Huang, G. W. Bailey, & A. R. Bowers (Eds.), *Metal speciation and contamination of soil* (pp. 1–33). Lewis Publishers and CRC.
- Hartikainen, H. (1986). Acid-and base titration behavior of Finnish mineral soils. *Z. Pflanz. Bodenkd.*, 149, 522–532.
- Hettelingh, J. P., Downing, R. J., & de Smet, P. A. M. (1991). Mapping critical loads for Europe, *CCE Technical Report* n° 1, Netherlands.
- Holmgren, G. S. (1967). A rapid citrate-dithionite extractable iron procedure. *Soil Science Society of America Journal*, 31, 210–211.
- Kabata-Pendias, A. (1995). Agricultural problems related to excessive trace metal contents of soils. In W. Salomons, U. Förstner, & P. Mader (Eds.), *Heavy metals. Problems and solutions* (pp. 3–18). Springer.
- Keeling, P. (1961). The examination of clays by IL/MA. *Transactions of the British Ceramic Society*, 60, 217–244.
- Loveland, P. J., & Whalley, W. R. (1991). Particle size analysis. In K. A. Smith, & C. E. Mullis (Eds.), *Soil analysis: Physical methods* (pp. 271–328). New York: Marcel Dekker.
- McBride, M. B. (2003). Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks. *Advances in Environmental Research*, 8(1), 5–19. doi:10.1016/S1093-0191(02)00141-7.
- Nicholson, F. A., Smith, S. R., Alloway, B. J., Carlton-Smith, C., & Chambers, B. J. (2003). An inventory of heavy metals inputs to agricultural soils in England and Wales. *The Science of the Total Environment*, 311, 205–219. doi:10.1016/S0048-9697(03)00139-6.
- Plaquart, P., Bonin, G., Prone, A., & Massiani, C. (1999). Distribution, movement and plant availability of trace metals in soils amended with sewage sludge composts: application to low metal loadings. *The Science of the Total Environment*, 241, 161–179. doi:10.1016/S0048-9697(99)00338-1.
- Prüß, A. (1997). Action values mobile (NH_4NO_3 -extractable) trace elements in soils based on the German national standard DIN 19730. Contaminated Soils 3rd International Conference on the Biogeochemistry of Trace Elements, Paris, (pp. 415–423).
- Ripley, E. A., Redmann, R. E., & Crowder, A. A. (1996). *Environmental effects of mining*. Delray Beach, Florida: St. Lucie.
- Ross, S. M. (1994). Retention, transformation and mobility of toxic metals in soils. In S. M. Ross (Ed.), *Toxic metals in soil-plant systems* (pp. 63–152). Chichester: Wiley.
- Simón, M., Ortiz, I., García, I., Fernández, E., Fernández, J., Dorronsoro, C., et al. (1998). El desastre ecológico de Doñana. *Edafología*, 5, 153–162.
- Simón, M., Ortiz, I., García, I., Fernández, E., Fernández, J., Dorronsoro, C., et al. (1999). Pollution of soils by the toxic spill of a pyrite mine (Aznalcóllar, Spain). *Science of Total Environment*, 242, 105–115.
- Stigliani, W. M. (1988). Changes in valued “capacities” of soils and sediments as indicators of non-linear and time-delayed environmental effects. *Environmental Monitoring and Assessment*, 10, 245–307.
- Ulrich, B. (1981). Ökologische Gruppierung von Böden nach ihrem chemischen Bodenzustand. *Z. Pflanzenernähr. Bodenkd.*, 144, 289–305.
- Van Breemen, N., Mulder, J., & Driscoll, C. T. (1983). Acidification and alkalization of soils. *Plant and Soil*, 75, 283–308.
- Vartanyan, G. S. (ed) (1989). The impact of mining on the environment, parts 1 and 2. In: Proceedings of an International Workshop at Tallinn-Leningrad, 18–25 June. Centre for International Projects GKNT, Moscow.